

UDC 666.1.056:504.2

COMPARATIVE ANALYSIS OF ENVIRONMENTAL RISKS PRESENTED BY GLASS-STRENGTHENING AGENTS

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Translated from Steklo i Keramika, No. 6, pp. 31–33, June, 2002.

Thermodynamic calculations are carried out, the range of contaminants which can be formed in strengthening of glass articles is identified, and their estimated concentrations levels are determined.

The process of surface strengthening of glass products is currently used in production of glass containers. This makes it possible to produce less heavy articles and to decrease the glass waste. Strengthening occurs as the glass surface at a temperature of 400–700°C contacts with the vapors of strengthening chemical agents, as a consequence of which the surface becomes coated with a thin film of tin or titanium oxides and the reaction products are released into the ambient medium [1]. The process of glass-container production, as a rule, lacks any purification of emissions from the strengthening unit.

An analysis of the existing practice of air monitoring in the work zone reveals that it only takes into account the possibility of hydrolysis of the strengthening agent with a release of such products as hydrogen chloride (danger class 2) and isopropanol (danger class 3). However, in the course of strengthening, one can expect not only the hydrolysis, but also the oxidation of the agent, which leads to the possibility of emitting other dangerous products, such as chlorine or carbon monoxide. Considering the wide application of the process of strengthening of glass containers, it is expedient to determine the range of products that may be formed and may affect the air of the work zone and the air of populated centers near glass factories.

Chemical agents are released into the ambient environment under different temperature conditions; accordingly, the composition of the reaction products differs. The prevailing process in storage, pouring, or emergency spilling processes is the hydrolysis of the strengthening agent by the water vapor contained in the atmosphere. The same occurs under technological evaporation, when the products at a temperature of 100–120°C penetrate into the workshop atmosphere as a result of imperfect airtightness of the equipment used. In a contact of the strengthening agent vapor with the glass products or in mixing with heated air at a temperature

above 400°C, a deeper destruction of the products should take place as a result of their oxidation.

The most common strengthening agents are GlasChem Hot 99 (trichlorobutyl tin as the active agent), KGU-2 (isopropyl titanate as the active agent), and tin tetrachloride.

The purpose of the present study is to determine the possible composition of the products emitted in hot strengthening of glass articles and to identify the safest potential product.

For each strengthening agent, a thermodynamic calculation of a composition approximately corresponding to the process conditions was carried out, i.e., 10 water molecules, 100 oxygen molecules, and 400 nitrogen molecules per molecule of strengthening agent. The temperature interval was selected so as to reflect in the calculation the temperature conditions corresponding directly to the glass-strengthening process and to the processes of storage, pouring, and technological evaporation of the strengthening agent. The pressure was taken equal to the atmospheric pressure. The calculation was performed on a PC using the Ivantanthermo program, and the calculation results took into account only those products whose content exceeded 10^{-7} weight parts. The calculation results are shown in Tables 1–3.

It can be seen that the contaminant compounds common for all strengthening agents which are formed at a temperature above 427°C, i.e., directly in strengthening of glass products, are nitrogen oxides arising as a consequence of air heating.

In using isopropyl titanate, only titanium dioxide was identified in the solid phase, which under industrial conditions should form an aerosol. Carbon dioxide and water arise in the gaseous phase within the entire temperature range. Since the rate of hydrolysis of isopropyl titanate significantly exceeds the oxidation rate of isopropyl titanate and isopropanol forming in the hydrolysis, one should expect the presence of isopropanol, instead of carbon dioxide, among the products arising in storage, pouring, and technological

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TABLE 1. Calculation Results of Destruction of Tin Tetrachloride (weight parts).
Estimated Composition: $\text{SnCl}_4 \cdot 10\text{H}_2\text{O} \cdot 100\text{O}_2 \cdot 400\text{N}_2$

Contaminant	Temperature, °C								
	27	127	227	327	427	527	627	727	827
N_2	7.55×10^{-1}								
O_2	2.13×10^{-1}	2.13×10^{-1}	2.14×10^{-1}	2.14×10^{-1}	2.14×10^{-1}	2.15×10^{-1}	2.15×10^{-1}	2.15×10^{-1}	2.15×10^{-1}
Cl_2	9.54×10^{-3}	9.41×10^{-3}	8.77×10^{-3}	7.30×10^{-3}	5.25×10^{-3}	3.30×10^{-3}	1.91×10^{-3}	1.09×10^{-3}	6.37×10^{-4}
H_2O	1.21×10^{-2}	1.21×10^{-2}	1.19×10^{-2}	1.16×10^{-2}	1.10×10^{-2}	1.05×10^{-2}	1.02×10^{-2}	9.99×10^{-3}	9.88×10^{-3}
HCl	8.36×10^{-6}	1.47×10^{-4}	8.04×10^{-4}	2.31×10^{-3}	4.42×10^{-3}	6.43×10^{-3}	7.85×10^{-3}	8.69×10^{-3}	9.14×10^{-3}
NO_2	—	—	—	1.72×10^{-7}	4.45×10^{-7}	9.09×10^{-7}	1.59×10^{-6}	2.48×10^{-6}	3.58×10^{-6}
NO	—	—	—	—	2.79×10^{-7}	1.99×10^{-6}	9.14×10^{-6}	3.10×10^{-5}	8.44×10^{-5}
HOCl	—	—	—	—	2.44×10^{-7}	4.94×10^{-7}	7.79×10^{-7}	1.06×10^{-6}	1.31×10^{-6}
SnCl_4	—	—	—	—	—	2.52×10^{-7}	4.12×10^{-7}	4.66×10^{-7}	4.37×10^{-7}
Cl	—	—	—	—	—	—	2.53×10^{-6}	1.00×10^{-5}	2.99×10^{-5}
ClO	—	—	—	—	—	—	1.18×10^{-7}	3.52×10^{-7}	8.32×10^{-7}
ClNO	—	—	—	—	—	—	—	1.00×10^{-7}	1.38×10^{-7}

TABLE 2. Calculation Results of Destruction of Isopropyl Titanate (weight parts).
Estimated Composition: $\text{Ti}(\text{OC}_3\text{H}_7)_4 \cdot 10\text{H}_2\text{O} \cdot 100\text{O}_2 \cdot 400\text{N}_2$

Contaminant	Temperature, °C								
	27	127	227	327	427	527	627	727	827
N_2	7.54×10^{-1}								
O_2	1.76×10^{-1}								
H_2O	2.19×10^{-2}	2.91×10^{-2}							
CO_2	3.55×10^{-2}								
NO_2	—	—	—	1.41×10^{-7}	3.64×10^{-7}	7.43×10^{-7}	1.29×10^{-6}	2.02×10^{-6}	2.92×10^{-6}
NO	—	—	—	—	2.53×10^{-7}	1.80×10^{-6}	8.28×10^{-6}	2.81×10^{-5}	7.63×10^{-5}

TABLE 3. Calculation Results of Destruction of Tin Tetrachloride (weight parts).
Estimated Composition: $\text{SnCl}_3\text{C}_4\text{H}_9 \cdot 10\text{H}_2\text{O} \cdot 100\text{O}_2 \cdot 400\text{N}_2$

Contaminant	Temperature, °C								
	27	127	227	327	427	527	627	727	827
N_2	7.53×10^{-1}								
O_2	2.00×10^{-1}	2.01×10^{-1}	2.01×10^{-1}	2.01×10^{-1}	2.01×10^{-1}	2.02×10^{-1}	2.02×10^{-1}	2.02×10^{-1}	2.02×10^{-1}
H_2O	1.75×10^{-2}	1.75×10^{-2}	1.73×10^{-2}	1.70×10^{-2}	1.65×10^{-2}	1.61×10^{-2}	1.59×10^{-2}	1.58×10^{-2}	1.58×10^{-2}
CO_2	1.18×10^{-2}								
Cl_2	7.14×10^{-3}	6.99×10^{-3}	6.33×10^{-3}	4.88×10^{-3}	3.06×10^{-3}	1.63×10^{-3}	8.14×10^{-4}	4.20×10^{-4}	2.32×10^{-4}
HCl	8.84×10^{-6}	1.55×10^{-4}	8.37×10^{-4}	2.33×10^{-3}	4.20×10^{-3}	5.67×10^{-3}	6.51×10^{-3}	6.91×10^{-3}	7.09×10^{-3}
NO_2	—	—	—	1.61×10^{-7}	4.17×10^{-7}	8.52×10^{-7}	1.49×10^{-6}	2.32×10^{-6}	3.36×10^{-6}
NO	—	—	—	—	2.70×10^{-7}	1.92×10^{-6}	8.85×10^{-6}	3.00×10^{-5}	8.16×10^{-5}
HOCl	—	—	—	—	2.25×10^{-7}	4.22×10^{-7}	6.25×10^{-7}	8.13×10^{-7}	9.84×10^{-7}
Cl	—	—	—	—	—	2.95×10^{-7}	1.65×10^{-6}	6.23×10^{-6}	1.81×10^{-5}
ClO	—	—	—	—	—	—	—	2.12×10^{-7}	4.87×10^{-7}

evaporation. Furthermore, the industrially produced isopropyl titanate KGU-2 contains up to 10 wt.% hydrocarbons that can be released in storage, pouring, and technological evaporation of the product.

When tin tetrachloride is used, only tin dioxide is identified in the solid phase, which under industrial conditions should form an aerosol. Chlorine and hydrogen chloride are present within the entire temperature range; however, it

should be taken into account that under low temperatures the rate of the hydrolysis of tin tetrachloride significantly exceeds its oxidation rate and the rate of hydrogen chloride formation in hydrolysis; consequently, one should expect the presence of hydrogen chloride instead of chlorine among the products arising in storage, pouring, and technological evaporation. At a temperature above 427°C corresponding to the glass-strengthening process, the products include hydrogen

chloride, tin tetrachloride, atomic and molecular chlorine, nitrosyl chloride, and ClO radical. When mixed with air of the working premises, tin tetrachloride has to hydrolyze with the formation of tin oxide and hydrogen chloride, whereas atomic and partly molecular chlorine, nitrosyl chloride, and ClO radical, which are highly active oxidizers, can react with organic products existing in the air of the working premises (lubricant and shrink-wrapping film vapors) with the formation of organochloric products. One cannot exclude the possibility of dioxin formation in this process.

In using trichlorobutyl tin, the composition of the products is similar to the composition of the products formed in using tin tetrachloride and is distinguished by the presence of carbon dioxide and the absence of nitrosyl chloride. However, at a temperature of 700–800°C, in addition to the products listed in Table 3, the formation of dioxin is theoretically possible in the strengthening zone. Furthermore, industrially produced trichlorobutyl tin as a rule contains up to 0.5 wt.% dichlorobutyl tin and up to 0.1 wt. % chlorotributyl tin, which are highly toxic nerve poisons [2]. These products as well as butane (one of the products of hydrolysis) can be emitted into air in storage and pouring of the agent.

The products whose presence may be expected in the air of the working zone depending on the agent used and the degree of their toxicity are listed below.

Products Formed As a Consequence of Using Various Strengthening Agents

Product	Danger class
<i>Tin tetrachloride</i>	
Tin dioxide (aerosol)	3
Hydrogen chloride	2
Chlorine	2
Nitrosyl chloride	Not determined
Nitric oxides	3
<i>Trichlorobutyl tin</i>	
Tin dioxide (aerosol)	3
Hydrogen chloride	2

Chlorine	2
Dichlorobutyl tin	2
Chlorobutyl tin	2
Butane	4
Nitric oxides	3
<i>Isopropyl titanate</i>	
Titanium dioxide (aerosol)	4
Isopropanol	3
Hydrocarbons	4
Nitric oxides	3

The danger class of the expected contaminant agents was determined according to a reference work [3].

As a consequence of the calculation performed, a range of the contaminants that may arise in strengthening of glass articles was established and their estimated concentration levels were determined.

With respect to the variety and general toxicity of the products generated in strengthening of glass articles, KGU-2 (isopropyl titanate as an active component) is the safest for the environment and the GlassChem Hot 99 agent (trichlorobutyl tin as an active agent) is the most dangerous.

To determine the composition of actually formed contaminants and to issue recommendations for monitoring of the air atmosphere, it is necessary to perform laboratory studies of the oxidation of strengthening agents under controlled conditions approaching the industrial conditions.

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